Resonant vibrational excitation of CO_2 by electron impact: Nuclear dynamics on the coupled components of the $^2\Pi_u$ resonance

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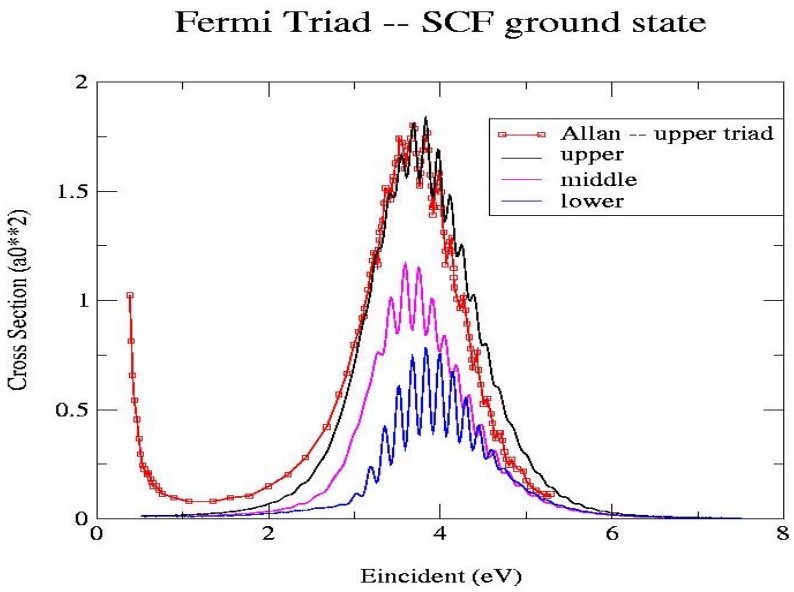
Although the principal features of low-energy electron-CO_2 scattering have been the subject of numerous experimental and theoretical investigations, recent laboratory studies[1] of resonant vibrational excitation have been carried out with unprecedented energy resolution and have revealed subtle details in the excitation cross sections whose origin and quantitative understanding pose serious challenges for *ab initio* theory.

The electron-CO_2 system is complicated for a number of reasons. The phenomenon of 'Fermi resonance', ie. an accidental degeneracy that occurs between certain zero-order vibrational states, leads to strong mixing between vibrational modes and necessitates a multi-dimensional treatment of the nuclear dynamics. The problem is further complicated by the fact that the negative ion "shape" resonance, which is degenerate in linear geometries ($^2\Pi_u$), splits into two non-degenerate surfaces upon bending which are strongly coupled by non-adiabatic Coriolis effects (Renner-Teller coupling).

I will describe the results of a fully *ab initio* study of resonant vibrational excitation of CO_2 by electron impact via the 3.8 eV "$^2\Pi_u$" shape resonance. The fixed-nuclei, electronic scattering problem is first solved, using the complex Kohn variational method, for a variety of symmetric-stretch geometries and for a range of bending angles. The fixed-nuclei cross sections are then analyzed to produce resonance parameters for both the $^2A_1$ and $^2B_1$ components of the resonance which, in linear geometry, correspond to the two components of the doubly degenerate $^2\Pi_u$ state of CO_2^-. The nuclear dynamics problem is solved by carrying out two-mode, time-dependent wavepacket studies on the coupled resonance surfaces in a complex local potential or 'boomerang' model.

These calculations have produced vibrational excitation cross sections that are in excellent agreement with experiment and reveal the origin of the subtle interference effects observed in the most recent experimental studies. To our knowledge, this represents the first time that all aspects of an electron-polyatomic collision, including not only the determination of the fixed-nuclei electronic cross sections, but also a treatment of the nuclear dynamics in multiple dimensions on coupled resonance surfaces, has been carried out entirely from first principles.

Cross sections for excitation of the [(2,0,0)/(1,2,0)/(0,4,0)] Fermi triad in CO_2 by electron impact. *Ab initio* results are compared with recent experiment.



1. M. Allan, Phys. Rev. Letts. **87**, 033201 (2001); *Photonic, Electronic and Atomic Collisions* (ICPEAC XXII), July 18-24, 2001, Santa Fe, NM, Book of Iinvited Papers (Rinton Press, 2002) p. 284.